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COLLOIDAL ASSEMBLIES EFFECT ON CHEMICAL REACTIONS(U)  
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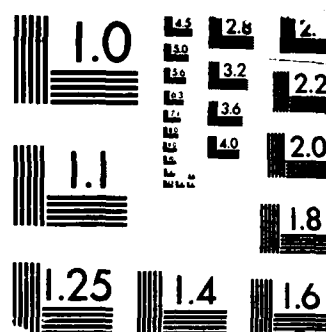
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COLLOIDAL ASSEMBLIES EFFECT ON CHEMICAL REACTIONS

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(1) In the period August-September 1985 the research carried out can be divided into the following parts :

1) PHOTODEGRADATION OF ORGANIC COMPOUNDS BY VISIBLE LIGHT.

Chloroaromatic derivatives ( compounds of relevant concern because some of them are bioaccumulative and persistent in the environment and also extremely toxic) were investigated.

Microbial degradation and naturally occurring hydrolysis require long periods; direct photodegradation requires high energy photons often leading to incomplete decomposition and , in some cases, to the formation of dangerous products.

Heterogeneous photo-assisted catalytic degradation by means of semiconductor particles has been applied to a variety of haloaromatic compounds ( see Table 1) . Various semiconductor slurries have been used and Figure 1 shows the results of light exposure of aerated aqueous solutions of 3,4-dichlorophenol. Inasmuch as naked  $TiO_2$  exhibited the highest efficiency in the photodegradation reaction, we have chosen  $TiO_2$  to investigate the decomposition of DCP and the series of haloaromatic compounds listed in Table 1. The presence of catalyst and light is essential for a rapid degradation. As well, oxygen and water are crucial ingredients for the reaction progress. As for the final products, analysis after long experiments (3 hours for DCP ) showed quantitative formation of  $CO_2$  and  $HCl$ .

Since substitution of  $TiO_2$  with  $Al_2O_3$  , or irradiation with light of wavelenght greater than the bandgap excitation of the semiconductor, leads to inefficient degradation, it is possible that organic radicals ( primary intermediates) are formed concomitant with the displacement of chlorine and formation of chloride ion. These radicals species can subsequently and rapidly produce hydroxy or dihydroxy aromatic intermediates which can be degraded further but at slower rates.

It is evident from the data of Table 1 that this semiconductor catalyst assisted photodegradation process can be applied to a wide variety of compounds even when present at very low concentrations. The degradation half life ( $t_{1/2}$ ) is only slightly affected by the increase in the halogen content as well as by the solubility of the compounds. Of interest, experiments have demonstrated that photodegradation proceeds at a significant rate also under direct sunlight.

Particular attention has been devoted to 2,4,5-T degradation. The identification of the intermediates has been accomplished through GC-MS technique (1).



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## 2) KINETIC INVESTIGATIONS OF THE EFFECT OF COLLOIDAL ASSEMBLIES AND SOLVENT COMPOSITION ON THE ELECTRON TRANSFER REACTIONS

The electron transfer kinetics between inorganic complexes (e.g.  $\text{IrCl}_6^{2-}$ ,  $\text{Mo}(\text{CN})_8^{3-}$ ) and benzenediols (catechol and substituted catechols) has been investigated in the presence of O/W microemulsions (water, NaCl 1% / toluene / 1-butanol / SDS). The rates of reactions are affected by the microemulsion concentration and composition. This effect is also dependent on the substituent (e.g. hydrophobicity) present on the aromatic ring (2).

The same reactions are actually investigated also in the presence of water/organic solvent mixtures (acetone, t-butanol, methanol).

Another investigation has concerned the degradation of chlorophenols by means of  $\text{H}_2\text{O}_2$  in the presence of  $\text{Fe}^{2+}$ . The final products, the parameters influencing the reactions have been assessed (3).

## 3) PROPERTIES OF AGGREGATES.

The formation of the ground state charge transfer complex between durene and chloranil has been investigated in  $\text{CH}_2\text{Cl}_2$  and in oil-in-water (O/W) microemulsions. The  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_2\text{Cl}_2$  /hexadecane microemulsion systems are stabilized by a cationic surfactant (hexadecyltrimethylammonium bromide) and 1-butanol as a cosurfactant. If the effective concentration in the oil phase ( $\text{CH}_2\text{Cl}_2$  /hexadecane) is accounted for, the equilibrium constant is not significantly changed with respect to the homogeneous  $\text{CH}_2\text{Cl}_2$  solution. The equilibrium of formation or dissociation of the complex is reached in less than  $1 \cdot 10^{-3}$  sec. (4).

# LIST OF PUBLICATIONS

1) M.Barbeni, E.Pramauro, E.Pelizzetti, M.Vincenti,  
E.Borgarello and N.Serpone - manuscript in preparation

2) C.Minero, E.Pramauro and E.Pelizzetti - manuscript in  
preparation

3) M.Barbeni; C.Minero, E.Pramauro, E.Pelizzetti, E.Borgarello  
and N.Serpone - manuscript in preparation

4) P.Infelta, R.Graglia and E.Pelizzetti - manuscript in  
preparation

## (2) RESEARCH PLANS

- Photodegradation of organic compounds by visible light.

Other haloaromatic compounds, such as PBC and dioxins, will be considered. Particular attention will be devoted in the investigation of the details of the reaction mechanism (adsorption-desorption process, kinetics, inhibition, nature of the semiconductor and its surface, detection of intermediates).

- Catalysis effects of transition metal ions complexes on reactions in homogeneous and heterogeneous media and in the presence of organised systems like micelles and microemulsions, will be explored, with particular attention to peroxide/metal ions degradative effect on organic compounds.

- The effect of organised assemblies and solvent composition on the electron transfer reaction between organic molecules and inorganic complexes will be examined.

- The physico-chemical properties of colloidal aggregates will be investigated.

(3) No significant administrative actions occurred during the period reported.

(4) -----

(5) Annex ( see attached sheets)

(6) No founds have have been received until now.

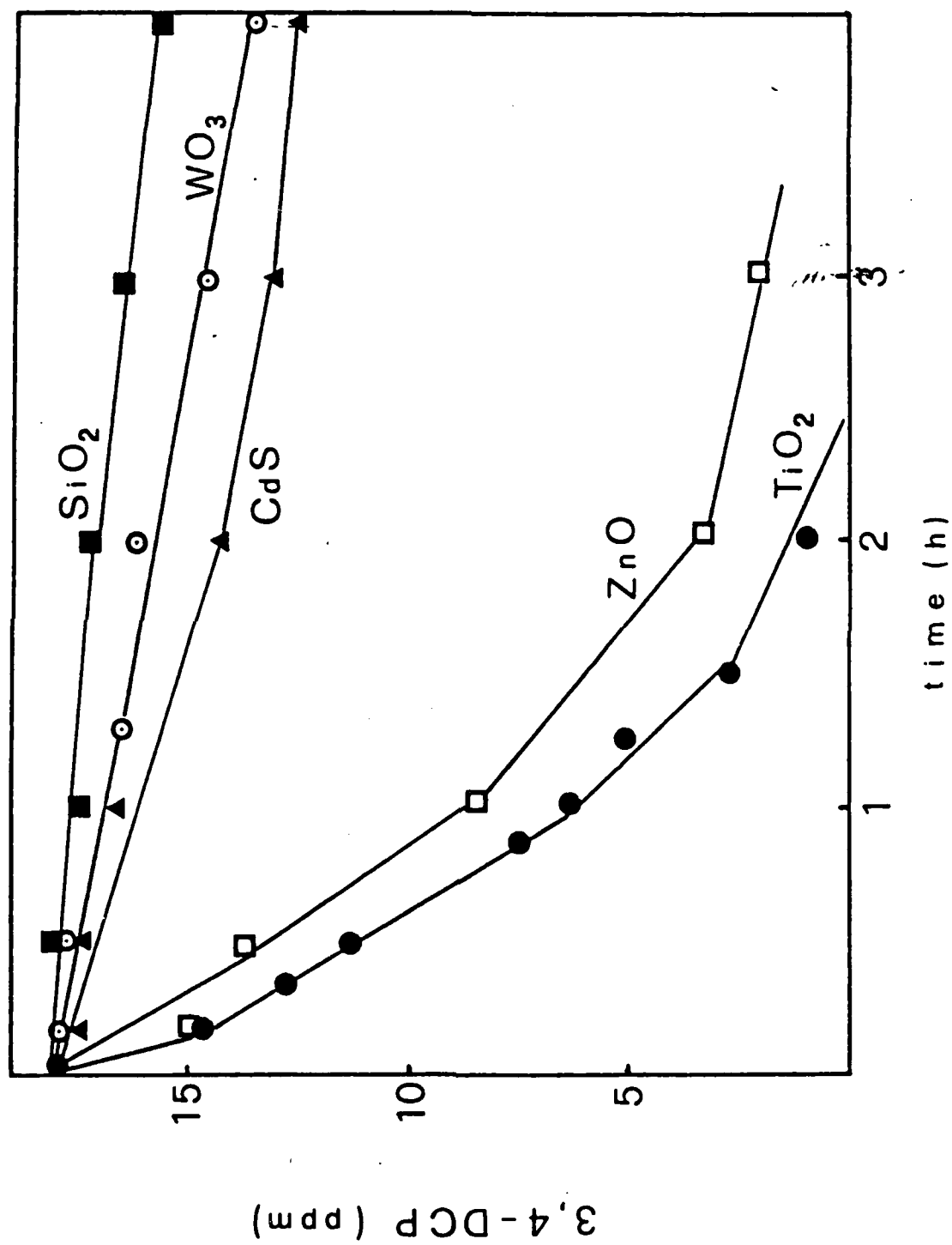
Table 1.- Half-lives for the Total Photodegradation of Contaminants Assisted by  $\text{TiO}_2$  on Exposure to Simulated Sunlight<sup>a</sup>.

COMPOUND	ABBREV.	CONCENTRATION (ppm)	pH	$t_{1/2}$ (min)
4-chlorophenol <sup>b</sup>	4-CP	6	3.0	14
3,4-dichlorophenol	3,4-DCP	18	3.0	45
2,4,5-trichlorophenol	2,4,5-TCP	20	3.0	55
Pentachlorophenol <sup>b</sup>	PCP	12	3.0	20
Sodium pentachlorophenate	NaPCP	12	10.5	15
Chlorobenzene	CB	45	2.5	90
1,2,4-trichlorobenzene	1,2,4-TCB	10	3.0	24
2,4,5-trichlorophenoxyacetic acid	2,4,5-T	32	3.0	40
4,4'-dichlorodiphenyltrichloroethane <sup>c</sup>	4,4'-DDT	1	3.0	46
3,3'-dichlorobiphenyl <sup>c</sup>	3,3'-DCB	1	3.0	10
2,7-dichlorodibenzo-p-dioxin <sup>c</sup>	2,7-DCDD	0.2	3.0	46

<sup>a</sup>: Concentration of catalyst, 2.0 g/l; aerated aqueous solutions; wavelength >330 nm.

<sup>b</sup>: Wavelength >310 nm.

<sup>c</sup>: Adsorbed on  $\text{TiO}_2$



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